EFFECT OF MILLING TIME AND MILLING MEDIA ON THE FORMATION OF CrSi$_2$ FROM THEIR CONSTITUENT ELEMENTS FOR THERMOELECTRIC MATERIALS

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ABSTRACT

A mixture of Cr-Si powder is mechanical alloyed through high energy ball mill (HEBM) at ambient temperature to prepare single phase CrSi2. CrSi2 is a candidate thermoelectric material for medium to higher range of working temperature. The composition chosen as Cr33Si68 and Cr32Si67 due to higher loss of Si as compared to Cr during MA by HEBM. The milled powder was characterized by X-Ray diffraction (XRD) at various time intervals to analyze the phase formation. Additionally, the particles morphologies and their interaction were also investigated by scanning electron microscopy (SEM). Result shows that formation of CrSi$_2$ phase starts after 25hours of milling although, longer milling time leads to transformation of CrSi$_2$ to CrSi and Cr$_5$Si$_3$phases. Some amount of tungsten contamination are found into the milled powder and are dependent on the milling time.

KEYWORDS: *Thermoelectric, Nano Structure, Mechanical Alloying, CrSi$_2$*

Original Article

INTRODUCTION

Globally, the demand of energy is increasing continuously. Till date, fossil fuels are the major energy sources to meet these worldwide demands but, the utilization efficiency of fossil fuels has virtually reached its limit. Environmental problems of gas emissions by fossil fuels and also the limitations of energy resources has resulted in extensive research into the development of new, clean and renewable energy sources. For example, approximately 40% of the total fuel energy is wasted from exhaust gas in internal combustion engines, 30% is used in engine coolant, 5% is lost as radiation and friction and only 25% is used for vehicle mobility and accessories [1]. Furthermore, around 60% of the energy extracted from power plants is lost as waste heat during its generation [2], and between 8 to15% is lost as heat in the electrical lines for its transport and transformationand rest of the electrical energy consumed in our houses[3]. Therefore, use of waste heat energy will be the most promising technique to achieve further energy demands.

Thermoelectric (TE)power generators have emerged as potential candidate for the conversion of waste heat energy into electrical energy. TE materials have immense potential to utilize the waste energy from different sources including automobile exhaust, different furnace fumes etc. [4].TE effect is quantitatively measured by dimensionless value which is generally called figure of merit and expressed as $ZT = S^2\sigma T/K_{Total}$.Here$ZT$ comprises of three key transport parameters (Seebeck coefficient$S$, electrical conductivityσ and total thermal

conductivityK_{Total}) as well as absolute temperature$T$[5]. $K_{Total}$is the sum ofthe electronic (K_E) and lattice (K_L) thermal conductivity. Only recently the $ZT \approx 1$ barrier has been broken, which generally is believed to be prerequisite for a commercial application. The challenge to develop TE materials with superior performance is to tailor the interconnected physical parameters *S*, *σ* and $K_{Total}$for a crystalline system. Thus, one seeks that, the material with high electrical conductivity, have high Seebeck coefficient with poor thermal conductivity.

State-of-the-art telluride or antimonide based TE materials are showing $ZT \approx 1$at room temperaturebut, these materials have major problems like toxicity, not widely available and less thermal stability at higher temperature [6-7]. Therefore, the new candidate materials which are non-toxic and abundant in the nature aremain focus of current research in the field of energy harvesting materials. Transition metal (TM) silicides are the promising candidate materialswhich includes beta- iron disilicide (β-FeSi$_2$), magnesium silicide (Mg$_2$Si), higher manganese silicide (MnSi$_x$)and chromium disilicide(CrSi2)[8].The CrSi$_2$is a potential thermoelectric material and has relatively high melting point (1763 K), high strength at elevated temperature and good oxidation resistance[9-11]. CrSi$_2$is reported as small band gap semiconductor with band gap of 0.29- 0.35 eV [12] and its *ZT* value is limited to 0.2 at 450 K [13-14]. This low *ZT* value is thought to be caused by bipolar conductionin low band gap materials, wherein the thermopower ($S^2\sigma$)decreases with increasing temperature [15].

Effective ways to improve efficiency of TE materials might be the nano structuring and band structure engineering. Nano structuring could lead to increase *S* due to quantum confinement and decrease $K_L$due to scattering of phonons at the interfaces, whereas doping could enhance thermopower due to band structure refinement[16-17]. The improvement of *ZT* value in mechanically alloyed CrSi$_2$is observed by doping the appropriate dopant in Si and Cr sites [6, 10, 13 and 14]. The density function theory also suggests that performance of CrSi$_2$at elevated temperature (900-1200K) can be improved by the doping the electron [18].

In the present work, the Cr and Si powder are selected as constitute elements to form CrSi$_2$nanosized powder using (HEBM). The phase analysis and morphology of powders interaction is studied by XRD and SEM for different time intervals. The effect of change in molar ratio (1:2 and 1:2.1) was also investigated to understand the compositional effect on the final product.

MATERIALS AND METHODS

The chromium and silicon powder were synthesized by MA method. The powder of Cr (5-6 µm)and Si (Analytical Reagent grade) with purity > 99 % were used as starting materials. The Cr and Si powder were weighed in the molar ratio of Cr:Si=1:2 and 1:2.1. These powders were milled in HEBM (Retsch: PM-400, Germany)using tungsten carbide vial (250 ml) and ball (φ 10mm) with rotation speed of 300 rpm for 100 hours using toluene. The ball to powder ratio (BPR) of 10:1 was used for the experiment. After 2 hours, 10 hours, 25 hours, 35 hours, 50 hours, 80 hours and 100 hours of milling, the powder samples were taken out from the vial for phase analysis. The room temperature XRD patterns were recorded on an X'pert Powder, X-ray diffractometer from PANalytical (The Nederland) using Cu Kα radiation (wavelength λ = 1.54178Å) for phase analysis. The particle morphology were analyzed by SEM (Zeiss EVO 18, UK).Quantitatively analysis of elements present on powder sample were analyzed by energy dispersive X-ray analyzer (EDAX).

RESULTS AND DISCUSSIONS

XRD pattern from starting mixture of Chromium and Silicon (1: 2 molar ratio) powder as a function of milling time is shown in figure 1. A significant decreasein intensities of Si peaks was observed after 2 h of milling as compared to Cr. This suggests that the Si atoms were dissolved into the Cr lattice to form an extended solid solution[19]. Similar observation was also published by Dasgupta*et al*. [20]. As milling time increases, the reductions in peak intensities of Cr and Siresults into the formation of $CrSi_2$ phase.The reduction on intensity of Cr peaks is due to sever plastic deformation of mixture after 10 h of milling.The peaks of $CrSi_2$ phase started during the 10 h milling and continued till 25 h whose intensity increases with time but, at the same time contamination of tungsten carbide (WC) also appears on XRD pattern. The WC contamination comesfrom themilling media due to the impact produced during milling between balls and inner wall of the vial.On further milling, Si particles are fragmented and chemical homogeneity can be attained, results into decrease in intensities of $CrSi_2$ and at the same time new CrSiphase formed.The broadening and decrease in intensities of the peaks gives information that crystalline size is reducing with increase the milling time. The peaks of Si falls more rapidly as compare to Cr peaks, that can be explained by the MA phenomenon as there is a tendency in initial stages that harder particles incrusted into softer matrix [21].

Milling was carried out till 100 h to investigate different types of phase formation process and also to determine the effect of contamination in the powder sample. On further milling up to total time of 80 h, $CrSi_2$and CrSiphase have not longer seen on the XRD pattern. A new phases Cr_5Si_3have observed at this stage. The transformation of $CrSi_2$to Cr_5Si_3 may be due to reaction between $CrSi_2$ and Chromium. After consuming all the Si, $CrSi_2$ can react with remained Cr to form Cr_5Si_3phase[22]. The sequence of phase formation in this study also satisfies the investigation done for by Colgan*et al*. for annealing of Cr and Si thin films [23]. After 100 h milling the powder mixture consisted of a majority of WC with small amount of Cr_5Si_3, Cr and CrSi. The sequence of phase formation on the XRD pattern have also observed for the Chromium and Silicon powder with molar ratio of 1:2.1 shown in Figure2.
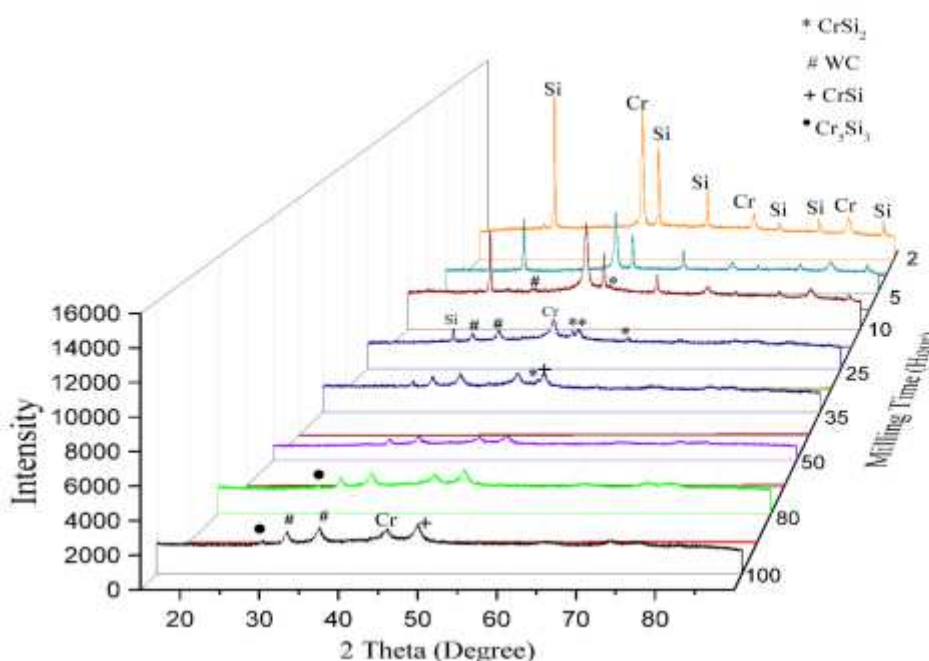

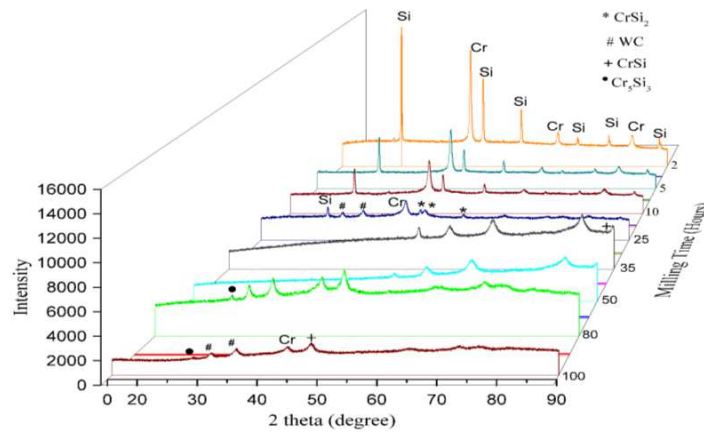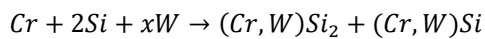**Figure 1: XRD Pattern of CrSi2 during the HEBM Steps**

Figure 2: XRD Pattern of CrSi2.1 during the HEBM Steps

EDAX of the milled powder for different time intervals showed presence of tungsten (W) contamination. Presence of W along with Cr in powder sample causes lowering of Cr : Si ratio and leads to the formation of higher Cr content (Cr_5Si_3) phase in alloyed sample. The possible reaction among Cr, Si and W may be:
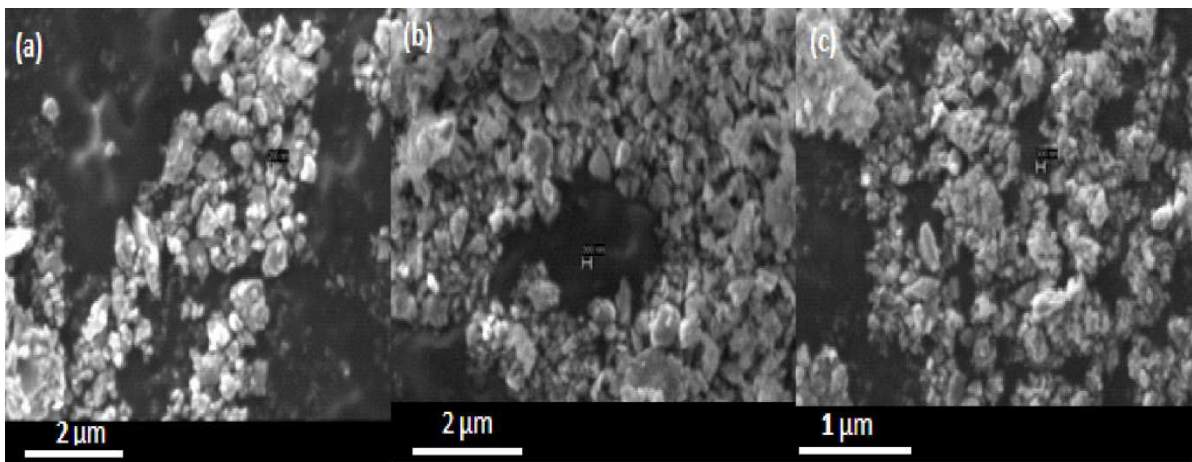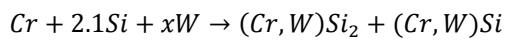
$$Cr + 2Si + xW \rightarrow (Cr, W)Si_2 + (Cr, W)Si$$

and,

$$Cr + 2.1Si + xW \rightarrow (Cr, W)Si_2 + (Cr, W)Si$$

Figure 3: SEM Fractrograph of CrSi2 milled Powders (a) 50 h (b) 80 h (c) 100 h

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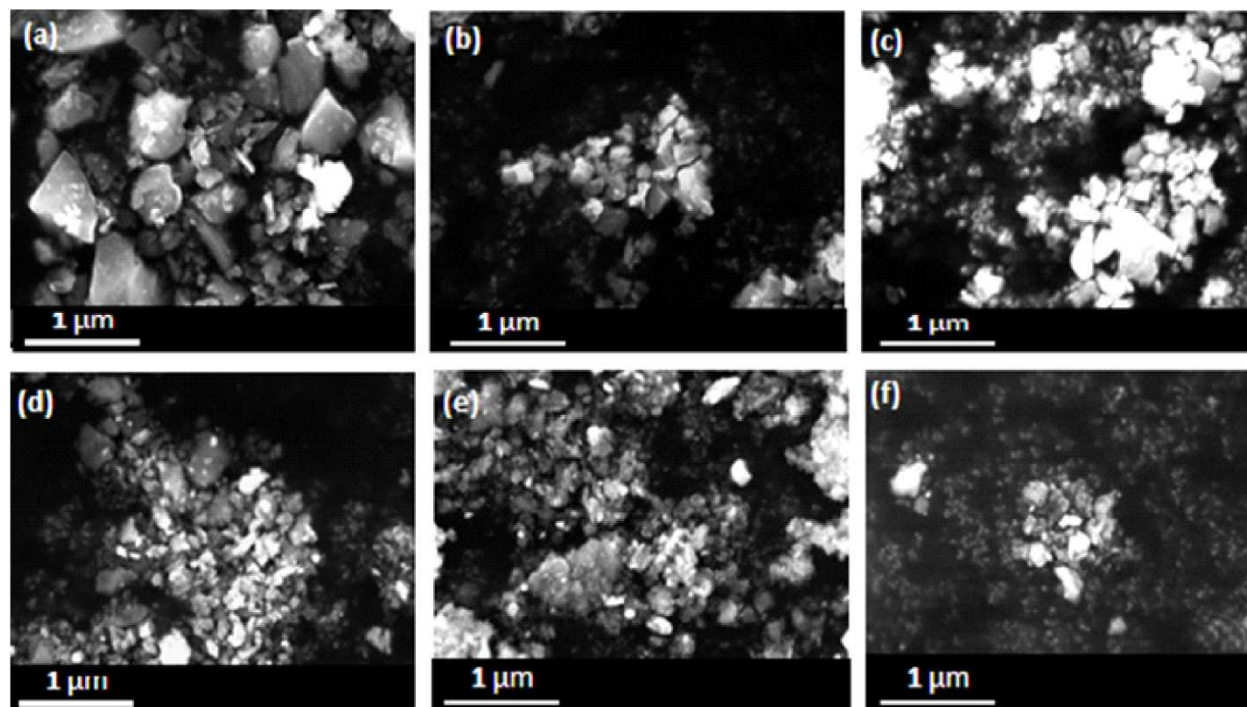**Figure 4: SEM Fractrograph of CrSi2.1 Milled Powders (a) 2 h (b) 25 h (c) 35 h (d) 50 h (e) 80 h and (f) 100 h**

Figure 3 and 4 shows the particle morphology and their interaction, investigated by SEM for molar ratio 1:2 and 1:2.1, respectively.The SEM image also suggests that agglomeration of powder particles increases with milling time. In early milling steps, the crystalline size were reduced (22 nm).After milling for 25, 35 and 50 h, an intense cold welding among the powder particles was noticed. This results into increase in crystalline size (28, 33.5 and 34 nm respectively), determined by using Scherrer equation. Milling the mixture for 80 h, fragmentation of welded particles started and reduction in crystalline size (28 nm) was achieved and for 100 h of milling increase in size occurs (34 nm) due to rewelding of the powder particles. Variation of crystalline size with milling time is shown in Figure 5.
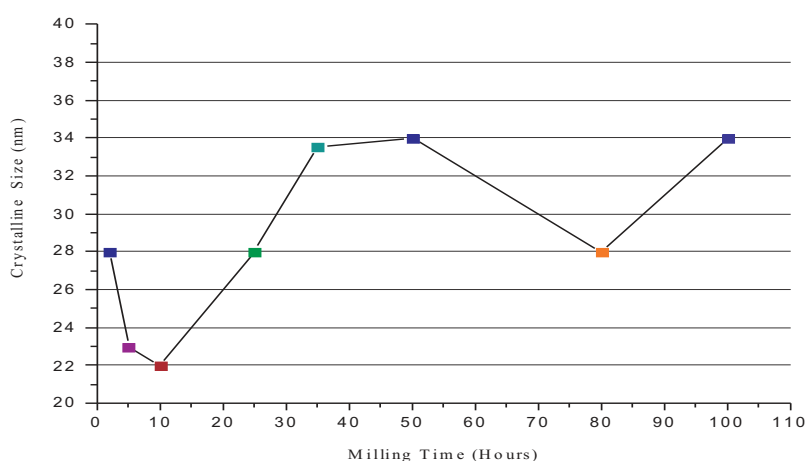

Figure 5: Milling Time verses Crystalline Size Variation

CONCLUSIONS

The MA of Cr and Si powders in molar ratio of 1:2 and 1:2.1 leads to formation of nanostructured $CrSi_2$. The obtained $CrSi_2$has hexagonal structure with space group $P6_222$ and crystalline size 28 nm. The $CrSi_2$ phase started for 10 h and continued to 35 h of milling. With further milling the reaction between $CrSi_2$ and Cr results into the formation of new phases ofCrSiand Cr_5Si_3.

The crystalline size variation with milling time, accurately defines the phenomenon of MA process that includes repeated welding, fracturing, and rewelding of powder mixture.

An intense tungsten contamination was observed through milling media and depends on the time of milling. Contamination in the Cr-Si powder mixture leads to formation of higher Cr contained phase.The W contamination in milled powder can be reduced by either decreasing the RPM of HEBM or by reducing the number of balls in each vial.

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